

# The effect of a secondary process on crystallization kinetics - Poly (ε-caprolactone) revisited

Phillipson, Kate; Jenkins, Michael; Hay, James

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## Accepted Manuscript

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Kate Phillipson, Michael J. Jenkins, James N. Hay

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**The Effect of a Secondary Process on Crystallization Kinetics –**

**Poly ( $\epsilon$ -caprolactone) Revisited**

by

**Kate Phillipson, Michael J. Jenkins and James N. Hay<sup>\*</sup>,**

The School of Metallurgy and Materials,  
College of Physical Science and Engineering,  
The University of Birmingham,  
Edgbaston,  
Birmingham B15 2TT, UK

Figures: - 9.

Tables: - 3

\*Corresponding Author

Tel: +44 121 414 4544      Fax: +44 121 414 5232

E-mail address: [j.n.hay@bham.ac.uk](mailto:j.n.hay@bham.ac.uk).

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**Kate Phillipson, Michael J. Jenkins and James N. Hay<sup>\*</sup>,**

The School of Metallurgy and Materials, College of Physical Science and Engineering, The University  
of Birmingham, Edgbaston, Birmingham B15 2TT, UK

**Abstract.**

It is suggested that the overlap of primary and secondary crystallization is a cause of the repeated observation of non-integer  $n$  values in polymer crystallization. The possibility that two concurrent crystallization processes occurring during the crystallization of poly ( $\epsilon$ -caprolactone), and polymers in general, may account for anomalous fractional values of the Avrami exponent, of no theoretical significance, is reconsidered using data from the recent evaluation of the kinetics of crystallization which placed emphasis on evaluating the secondary crystallization stage.

In general constant  $n$  values in excess of that expected for the crystallization mechanisms could readily be interpreted in terms of the additional crystallinity developed by the secondary process and these values increased commensurate with the rate constant of secondary crystallization.

**Keywords:**

Poly ( $\epsilon$ -caprolactone); crystallization kinetics; concurrent processes; diffusion control.

## 1. Introduction

The presence of primary and secondary crystallizations occurring together rather than consecutively has been shown to account for anomalous fractional values of the Avrami exponent,  $n$ , in the crystallization of poly (ethylene terephthalate) [1]. Constant values in excess of those expected for the crystallization mechanisms are due to the additional crystallinity developed by the secondary process. In order to consider the generality of this phenomenon recent evaluation of the kinetics of crystallization of poly ( $\epsilon$ -caprolactone), which placed emphasis on measuring the secondary crystallization separately and in detail [2, 3] have been reconsidered in the light of these observations.

Recently [2-5] secondary crystallization has been considered to involve diffusion controlled thickening of lamellae, the structural units of spherulites. The radial growth of the lamellae occurs linearly with time until the spherulites impinge with one another; radial growth is nucleation controlled in that the rate increases with the undercooling from the melting point. In contrast the lamellae thicken perpendicular to the lamellar growth direction by the production of overgrowths on the “fold surface”, develop with the square root of time by diffusion control of localized small chain segments and the rate of thickening increases with temperature [2]. Since the lamellae produced in the initial stages of the crystallization are thicker and the lamellae

decrease in thickness towards the outside of the spherulite [7] the thickening process occurs as soon as the lamellae develop from the initial stage of crystallization.

These two processes account for primary and secondary crystallization of polymers and have been combined into a composite rate equation [1], relating the overall fractional crystallinity,  $X_t$ , to lapsed time;

$$X_t = X_{p,inf}(1 - \exp(-Z_p t^n))(1 + k_s(t^{1/2})) \quad [1].$$

where  $X_{p,inf}$  is the final fractional crystallinity achieved by the primary process,  $Z_p$  a composite rate constant,  $t$  the lapsed time, and  $n$  the integer constant for the primary process. The diffusion rate constant for secondary crystallization is  $k_s$ . This paper reconsiders the crystallization kinetics of poly ( $\epsilon$ -caprolactone) in order to consider if the equation more accurately describes the overall dependence of the fractional crystallinity with time and explains the constant non-integer values of  $n$  commonly observed in the crystallization of many polymers.

PCL is a particularly useful polymer to study since its crystallization behaviour has been widely studied by many techniques and fractional  $n$  values invariably reported when the Avrami equation has been adopted to analyze the time dependence of crystallization [8-12].

## 2. Experimental

Polymer characteristics and experimental procedures are as outlined in detail elsewhere [2, 3].

### 3. Results and Discussion.

#### 3.1. Rate Equation for Secondary Crystallization.

It is inherent in the derivation of eq. 1 that the extent of secondary crystallization is limited to regions of the sample already confined within the boundaries of the spherulite and the secondary process continues to increase with the square root of the lapsed time after the primary stage is complete.

At values of  $X_t > X_{p,inf}$  the exponential function is equal to zero and the increase in fractional crystallinity with time is then,

$$X_{s,t} / X_{p,inf} = (1 + k_s t^{1/2}) \quad (2)$$

The data measured previously [3] for the crystallization of PCL was analyzed after the primary process had ended to confirm the dependence of  $X_{s,t}$  on  $t^{1/2}$  the  $X_t$  v.  $t$ . Plots of  $X_{s,t}/X_{p,\infty}$  against  $t^{1/2}$  were linear with intercepts of 1.00 and slope of  $k_s$ , see Figure 1. The rate parameters for the secondary crystallization are listed in Table 1. The relative degree of fit of the data to was gauged from,  $R^2$ , which were about 0.91-0.99. There was a general trend for  $k_s$  to increase with temperature consistent with diffusion control of secondary crystallization. This process obeyed an Arrhenius dependence on temperature, i.e.

$$k_s = A \cdot \exp(-\Delta E/RT_c) \quad (7)$$

where  $A$  is a pre-exponential factor,  $\Delta E$  the activation energy for viscous flow,  $R$  the gas constant and  $T_c$  the crystallization temperature. The activation energy was

determined to be  $40 \pm 10 \text{ kJ mol}^{-1}$ , see Figure 2 and compares with  $35 \pm 5 \text{ kJ mol}^{-1}$

determined previously for the activation energy of diffusion of PCL [2].

The large uncertainty in the activation energy reflects the small temperature range studied and the small change in fractional crystallinity associated with secondary crystallization.

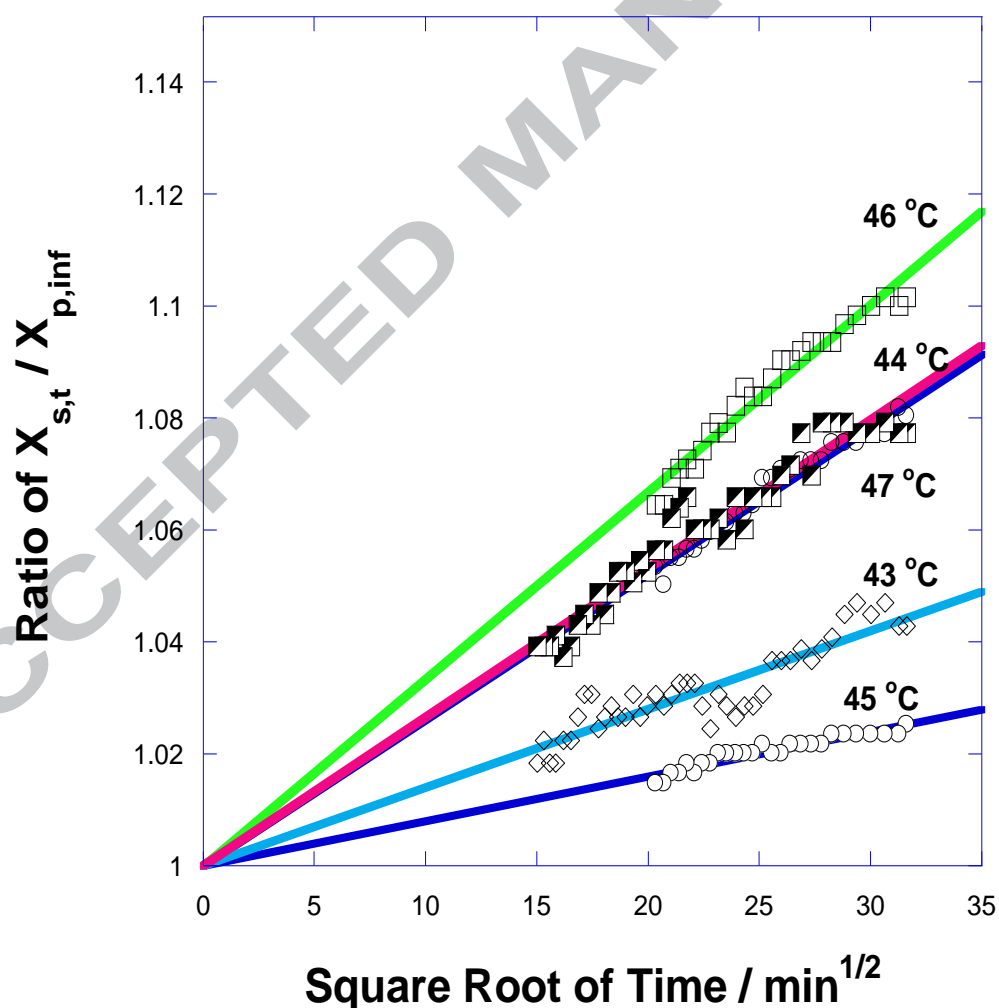


Figure 1.  $X_{s,t}/X_{p,\infty}$  against square root of crystallization time.



**Table 1. Secondary Crystallization Rate Parameters**

Crystallization Temperature / °C	Fractional Crystallinity $X_{p,inf}$	Rate Constant $k_s / \text{min}^{-1/2}$ $\times 10^3$	Relative Degree of Fit $R^2$
47	0.23	$2.60 \pm 0.30$	0.99
46	0.54	$3.40 \pm 0.30$	0.96
45	0.39	$1.00 \pm 0.30$	0.92
44	0.52	$2.60 \pm 0.30$	0.99
43	0.46	$1.33 \pm 0.30$	0.94

### 3.2. Primary Crystallization Kinetics;

The fractional crystallinity-time dependence was calculated using the parameters listed in Table 1 for each crystallisation temperature in eq. 1 and is compared with the experimentally determined dependence in Figure 2. The half-lives were taken to be the time at which  $X_t = X_{p,\infty} / 2$  and  $Z_p$  was calculated from  $Z_p = 0.693 / (t_{1/2})^n$ . The  $n$  value of 2.0 was selected for the growth of discs limited in thickness by the film samples; in this way there were no adjustable parameters.

The change in crystallinity with log time, see Figure 2, precisely followed that observed previously [3] as measured by FTIR spectroscopy. It exhibited an initial period with an exponential increase followed by a linear increase with log time attributed to primary and secondary crystallization.

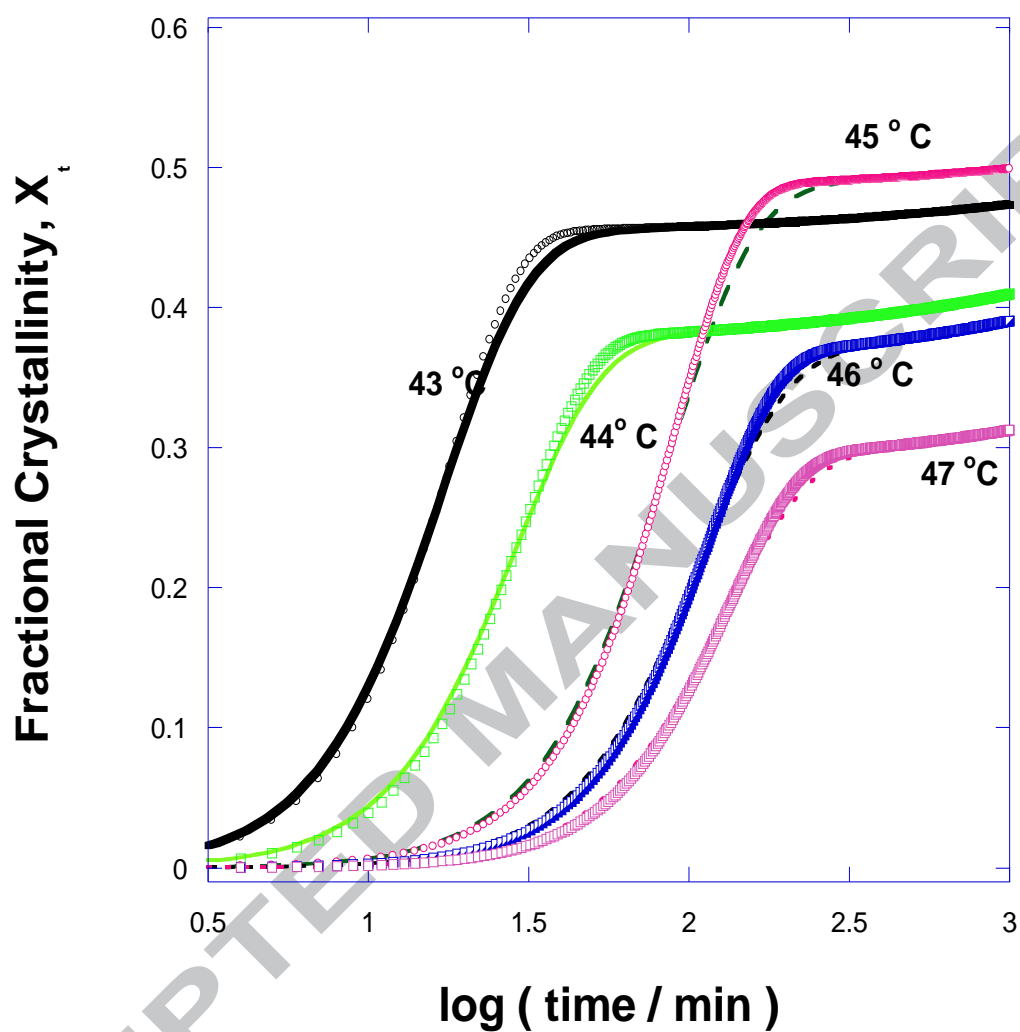


Figure 2. Fractional Crystallinity-Time Dependence as calculated by eq. 1.  
Calculated - lines: experimental - open symbols.

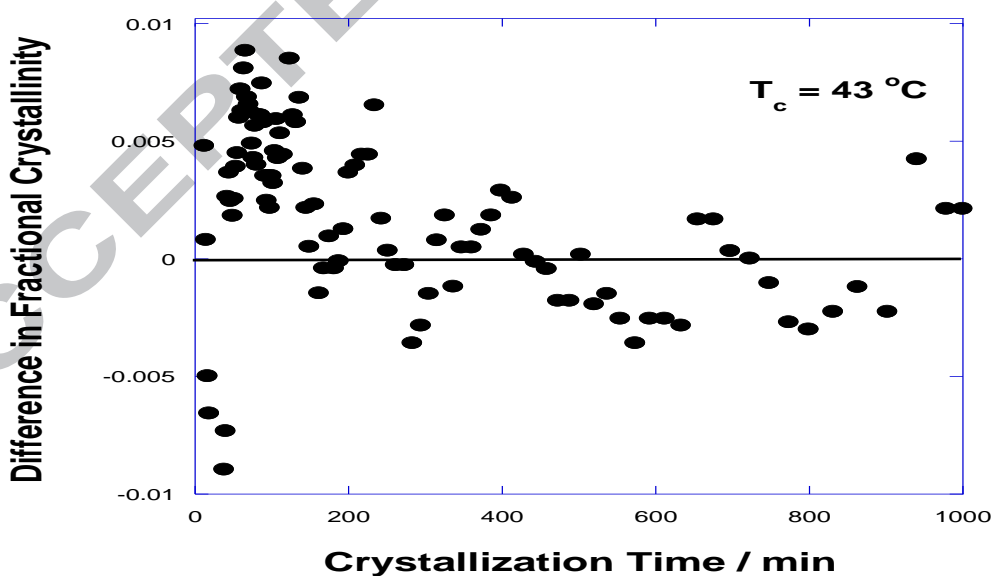
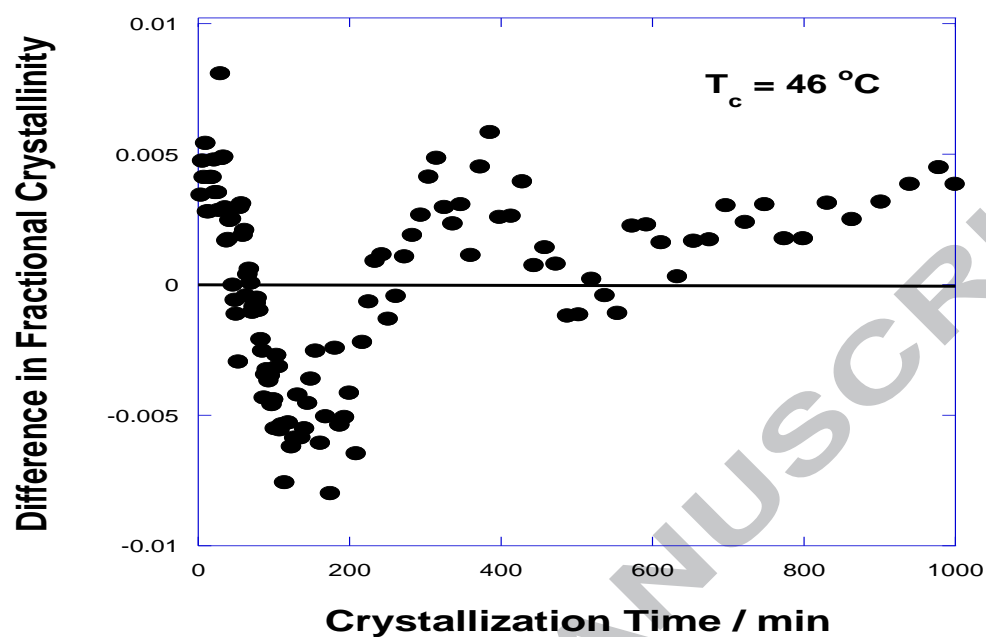


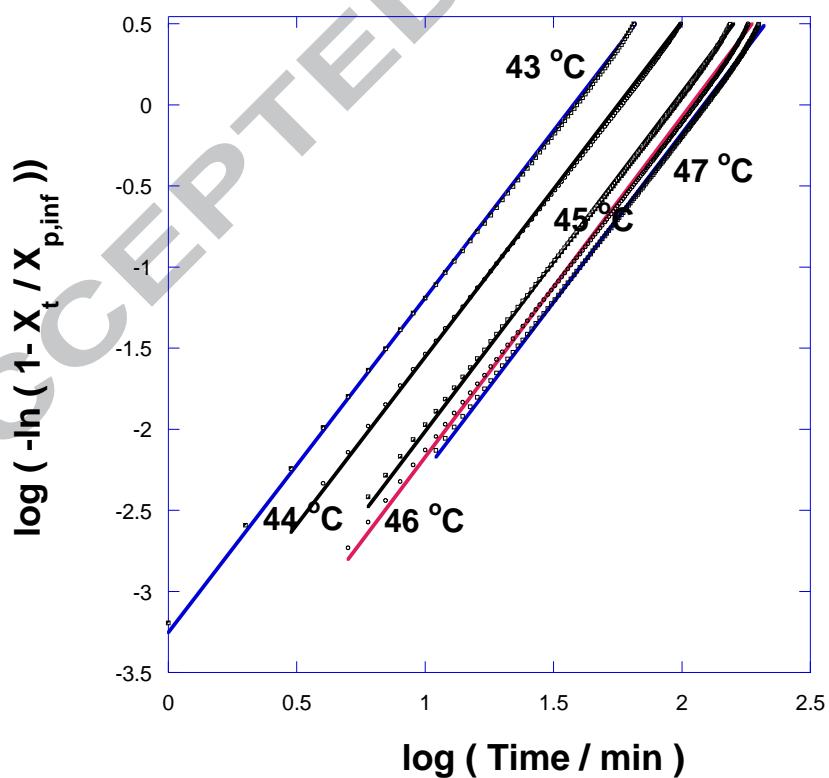
Figure 3. The Difference between Experimental and Calculated Fractional Crystallinities with Crystallization Time.

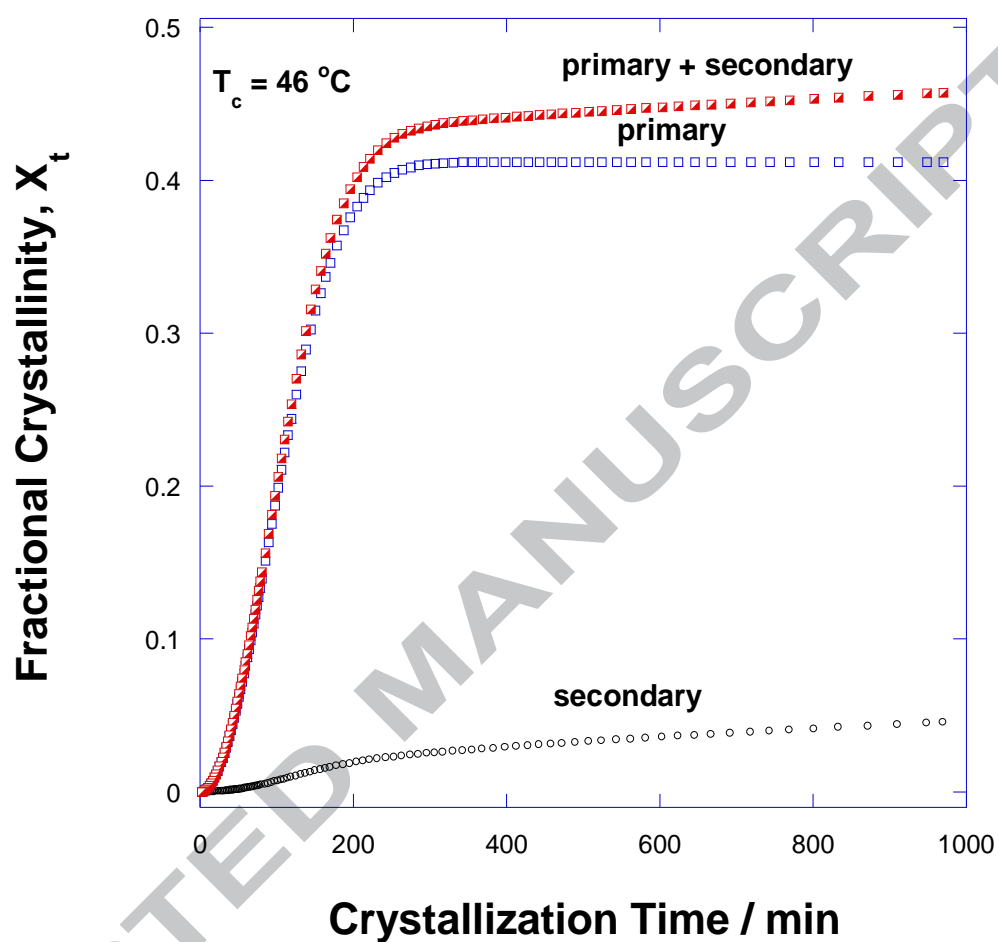
The fit of eq. 1 to the experimental data is more clearly seen from the difference in observed and calculated fractional crystallinities with time as shown in Figure 3 in that the calculated fractional crystallinity was subtracted from the experimental value at the same crystallization time. Differences were  $\pm 0.005$  overall which was similar to the accuracy in measuring  $X_t$  experimentally as determined previously [3].

The calculated curves were further analysed as previously assuming that primary crystallization occurred first followed by secondary at  $X_t = X_{p,inf}$  to determine the  $n$  value from the slope of  $\log(-\ln(1-X_t/X_{p,inf}))$  against  $\log$  time, see Figure 4; the rate parameters determined from the plots are listed in Table 2 along with the relative goodness of fit,  $R^2$ , (the least squares fit of the straight line). Although eq. 1 was an excellent fit to the experimental data all the  $n$  values were constant but fractional outside the error range. The values decreased with decreasing secondary rate constant suggesting that there was an additional contribution from secondary crystallization which decreased with the value of the rate constant,  $k_s$ . It can be seen from Figure 5 where the two components have been separated into primary and secondary crystallization that the later contributes about 10% to the overall fractional crystallinity; this additional contribution raised the  $n$  value to 2.10.

Table 2. Rate Parameters.

Crystallization Temperature / °C	Exponent n ± 0.05	- Log (Z <sub>p</sub> ) / min <sup>-n</sup>	Relative Degree of Fit R <sup>2</sup>
47	2.11	4.34	0.96
46	2.10	4.27	0.96
45	2.09	4.10	0.96
44	2.06	4.05	0.98
43	2.07	3.62	0.97

Figure 4. Determination of the  $n$  Values.



**Figure 5. Separation of the observed Fractional Crystallinity,  $X_t$ , into Primary and Secondary Components.**

### 3.1. The effect of the secondary crystallization rate constant on the n value.

In order to determine the effect of secondary crystallization on the value of n the secondary rate constant,  $k_s$ , was systematically altered while the primary rate parameters kept constant. The fractional crystallinity was calculated using equation 1 with  $X_{p,\infty} = 0.50$ , and a half-life of 200 min. The integer value of n was chosen to be n=2.00 in line with the crystallization model of expanding pre-determined discs, as adopted by Avrami [7] and observed experimentally.

The rate constant for secondary crystallization was changed systematically from 0.00 to  $0.10 \text{ min}^{-1/2}$ , see Figure 6, and the resulting increase in secondary crystallinity with increasing rate constant can be seen in Figure 7. It was clear that as the rate constant increased secondary crystallization made a greater contribution to the overall crystallinity during the initial stages and increasingly dominates towards the end of the primary process; n values were determined as above using  $X_{p,\infty}$  equal to 0.500. In every case n was constant and fractional above 2.00, its value increasing with  $k_s$ , see Figure 8.

Similar increases in n values were observed for the same secondary rate constants using n values of 3.0 and 4.0 such that it was concluded that secondary crystallization did account for the observed fractional n values observed in the primary crystallization of PCL. However, they were never greater than 0.3 above the integer value predicted for the crystallization mechanism [7], see Figure 8.

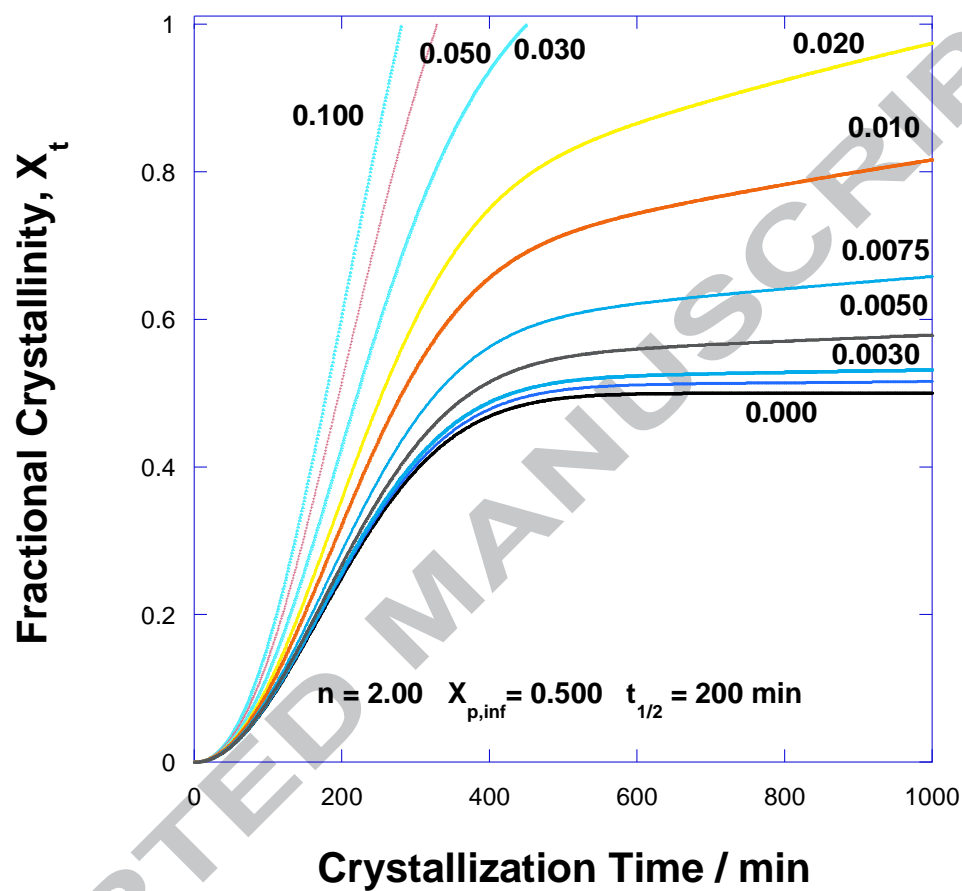


Figure 6. The effect of the secondary rate constant,  $k_s$ , on the overall crystallization time dependence.

(Each curve is designated by  $k_s$  value in  $\text{min}^{-1/2}$ )



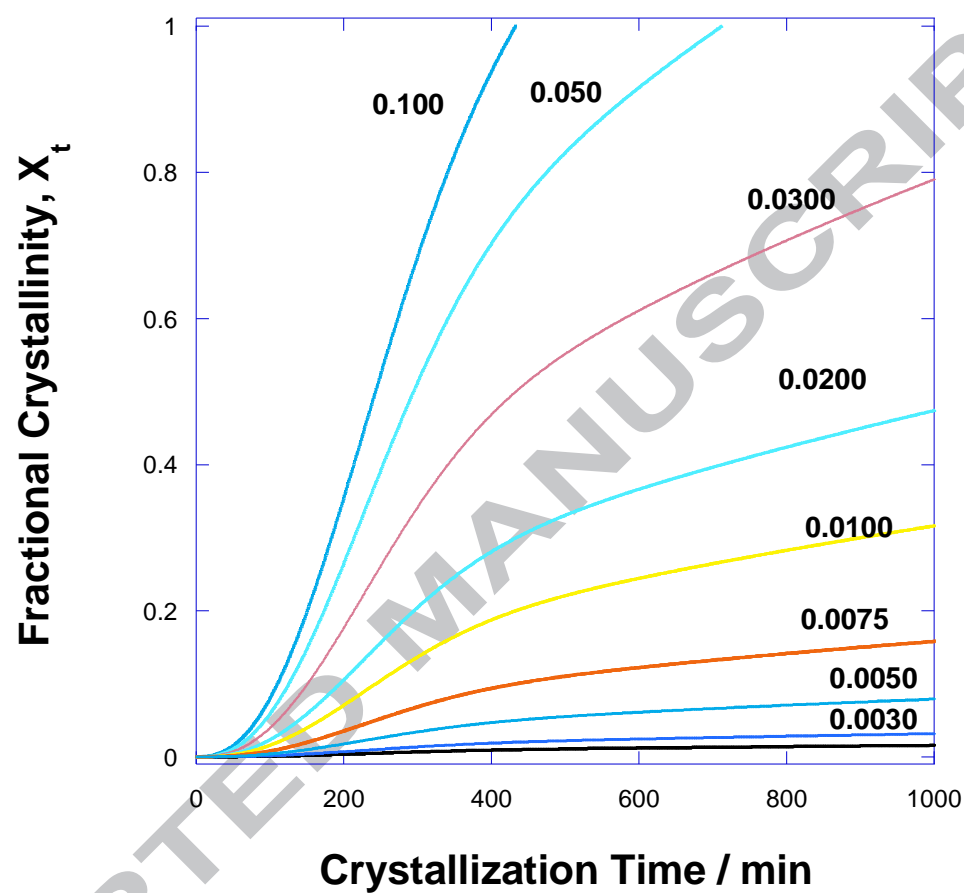


Figure 7. The dependence of the secondary crystallization on the rate constant,

$k_s$ .

(Each curve is designated by  $k_s$  value in  $\text{min}^{-1/2}$ )

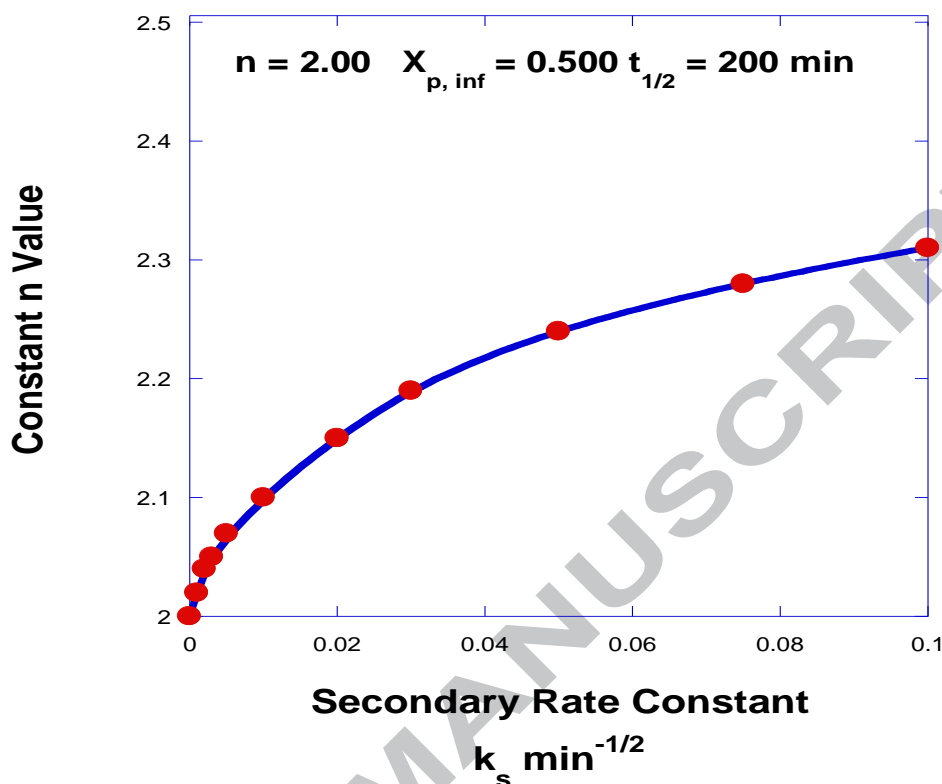


Figure 8. The effect of changing secondary rate constant on the n value.

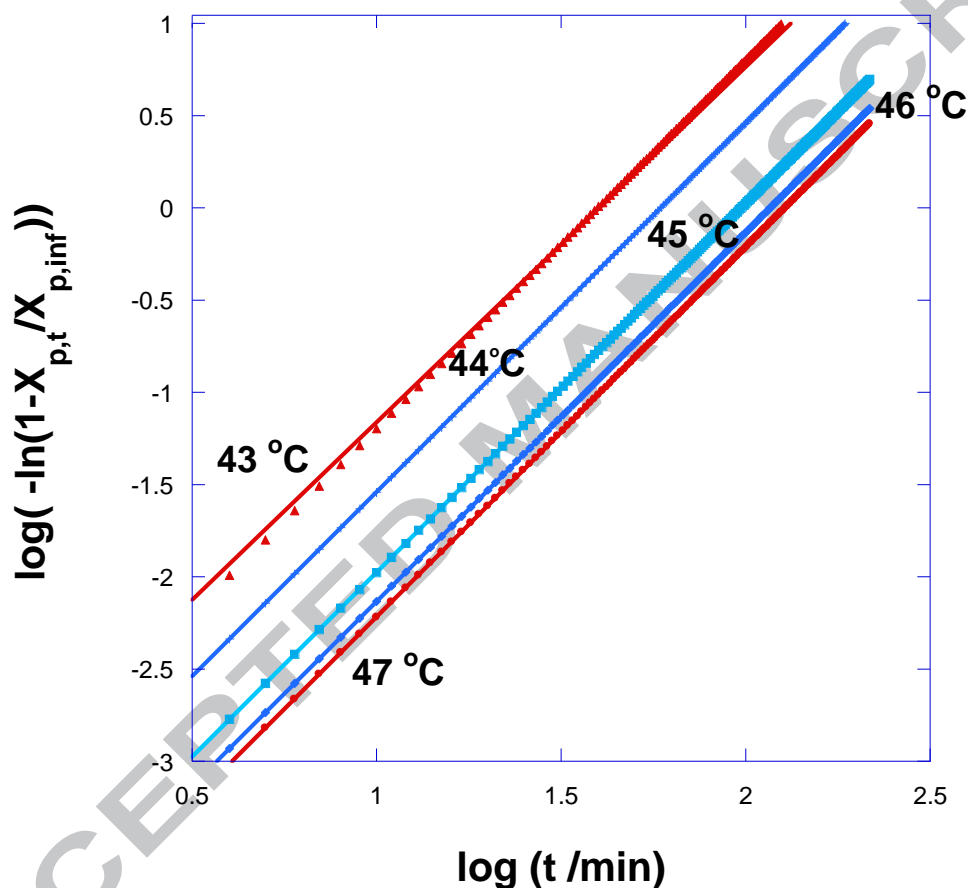
#### 4.0 Conclusions

It is obvious from Figures 6, 7 and 8 that on increasing the secondary crystallization rate constant, from 0.00 to 0.10  $\text{min}^{-1/2}$ , there is a greater contribution to the overall fractional crystallinity from the secondary process and progressive deviation from the Avrami equation. The rate parameters of the primary process cannot be determined by analysis of the time dependence of the measured fractional crystallinity alone. However, the fractional crystallinity contribution from primary crystallization,  $X_{p,t}$ , can be determined directly from equation 1, in that

$$X_{p,t} = X_t / (X_{p,\text{inf}} (1 + k_s t^{1/2}))$$

$$\text{And } X_{p,t} = X_{p,\text{inf}} (1 - \exp(-Z_p t^n)) \quad (8)$$

$$\text{Such that } \log(-\ln\{1 - X_{p,t}/X_{p,\text{inf}}\}) = n \cdot \log(t) + \log(Z_p)$$



**Figure 9. Analysis of primary crystallization.**

Linear plots of  $\log(-\ln\{1 - X_{p,t}/X_{p,\text{inf}}\})$  against  $\log(t)$  for the primary fractional crystallinity were obtained with slopes of  $n$  equal to 2.0, see Figure 9 and Table 3, as required by Avrami for the linear radial growth of predetermined discs. The goodness of fit of the least square lines were greater than 0.99, see Table 3. In this analysis no adjustable parameters were used as  $X_{p,\text{inf}}$  was measured as described above.

To conclude it would appear that fractional constant  $n$  values as observed previously in the crystallization of PCL arose from the incorrect assumption that secondary crystallization developed at a later stage in the crystallization and the initial stages were due entirely to the development of primary crystallization.

Methods have been developed to separate these two processes and enable each to be analyzed separately. If this procedure is carried out integer values of  $n$  are observed which have meaning within the mechanisms suggested by Avrami [7].

**Table 3. Primary Rate Parameters.**

<b>Crystallization Temperature / °C</b>	<b>Exponent  n</b>	<b>Half Life  (<math>t_{1/2} - t_i</math>) / min</b>	<b>Induction Time / min</b>	<b>Goodness of Fit  R<sup>2</sup></b>	<b>-log (Z<sub>p</sub>)</b>	<b>X<sub>p,∞</sub></b>
47	2.00	107	38	0.995	4.33	0.23
46	2.02	97	21	0.999	4.24	0.54
45	2.00	81	18	0.999	3.99	0.39
44	2.04	33	12	0.992	3.36	0.52
43	2.00	25	6	0.997	2.04	0.46

### **Acknowledgements**

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**Highlights (for review)**

- The Avrami equation has been modified to incorporate secondary crystallization.
- The presence of secondary crystallization accounts for fractional constant  $n$  values.
- Secondary crystallization develops with the square root of time involving diffusion of small segments of the chain.
- Primary crystallization involves the linear growth of lamellae with time involving long entangled chain segments.

## CRYSTALLIZATION KINETICS

**Total Crystallinity = Primary + Secondary**

$$X_t = X_{\infty} (1 - \exp(-Zt^n)(1 + k_s t^{1/2}))$$

**Primary**

**Secondary**

**Kinetic analysis involves separating Secondary from**

**Primary Crystallization**

**and plotting**

**$\log (-\ln (X_t / X_{\infty} (1 + k_s t^{1/2})))$  against  $\log t$ .**